Synthesis and Nonlinear Optical Characterization of Certain Chalcogen Based Nanostructures

Among several innovative materials explored by the scientific community, chalcogen based nanostructures stand out due to their applications in solar energy conversion, optoelectronic devices, cellular imaging and ultrasensitive detection. These materials also have great significance due to the purely fundamental specific properties. One of the chalcogen elements, Selenium (Se), known as elemental semiconductor, exhibits both photovoltaic and photoconductive properties. Selenium nanocrystals on the other hand have potential applications in rectifiers, solar cells, xerography, X-ray photoconductor and are attractive due to their ability to form variety of allotropic forms. Transition metal chalcogenides, viz. oxides, sulfides, selenides and tellurides hold an important position due to their ability to form semiconducting quantum dots (QDs) useful for luminescence, photo-conducting, sensing and nonlinear optical applications. Earlier research works were mostly devoted to developing nanoparticles of II-VI and III-V semiconductors while I-VI semiconductor materials such as Ag_2S and CuS were not equally explored to produce efficient nanomaterials with fascinating properties. In fact the nonlinear optical absorption, particularly ultrafast optical nonlinearity in different Se allotropric nanostructures and Ag_2S/CuS nanoparticles systems, is not well established.

Interaction of electromagnetic radiation with matter has been a fertile area to produce fruitful results from early days. Under ordinary circumstances, the optical properties of a material do not depend on the intensity of the light incident on it. However, at high intensities, materials become optically nonlinear. Interesting developments in the field of intensity dependent light matter interactions came with the advent of lasers. With the dawn of laser technology, interaction of intense laser pulses with materials, particularly with nanostructures, is being greatly

exploited to develop highly nonlinear materials, and to provide rich scientific insights. Conversely, the universal application of intense laser beams in a variety of applications brings about several associated dangers including damage to optical sensors, and therefore, development of efficient optical limiting materials is a demanding requirement.

The present thesis is an investigation of the interaction of moderately intense nanosecond and femtosecond laser pulses with certain chalcogen based nanomaterials. The synthesized nanomaterials are studied for their morphological, crystalline, microstructural, spectroscopic and nonlinear optical properties.

The thesis is divided into seven chapters and the chapterwise summary of the same is given below.

Chapter 1 gives a general introduction to chalcogenide based materials, and provides a review on Se nanostructures, Ag_2S and CuS nanoparticles, semiconductor- semiconductor nanocomposites and alloys. Various technological applications of chalcogenide based semiconductor nanoparticles are also briefly explained. In addition, a general introduction to the nonlinear optical properties of matter in a strong laser field is presented. A brief discussion on various nonlinear absorption processes and an overview of the generation of ultrafast laser pulses are mentioned. Experimental technique employed for nonlinear transmission measurements and applications of optical limiters are also discussed. Evolution of optical nonlinearity from nanosecond to femtosecond excitation domains is briefly discussed in the later section. The organization of the thesis and the aim and objective of the research work are also touched upon at the end of the chapter.

Chapter 2 discusses the optical nonlinearity of two different forms of selenium nanostructures; namely, crystalline selenium nanowires and amorphous selenium nanoparticles. The nanostructures were synthesized by a simple chemical route, and characterized by XRD, absorption spectra

and photoluminescence spectra. Optical nonlinearity studies were performed with optical excitation in two distinct time regimes: (i) ultrafast excitation using 100 femtosecond laser pulses, and (ii) short-pulse excitation using 5 nanosecond laser pulses. The underlying mechanisms of nonlinearity are different in these two regimes and are discussed in detail. For instance, while intensity-dependent instantaneous nonlinearities are prominent in the ultrafast excitation regime, fluence-dependent accumulative nonlinearities dominate the short-pulse excitation regime. The coefficients for saturable absorption, two-photon absorption, three-photon absorption, and excited state absorption in the Se nanostructures have been estimated and presented. These results show that these materials are efficient optical limiters with potential applications in laser safety devices.

Chapter 3 provides measurement of the enhanced ultrafast optical nonlinearity of cubic and amorphous Se doped silica matrices. The average size of the Se semiconductor estimated from the TEM micrograph and the crystalline nature examined form SAED pattern are presented. The FTIR spectra of Se doped silica are studied for structural characterization. The optical band gaps of both allotropic forms of Se nanoparticles are calculated from the absorption spectrum. Among the two allotropes only cubic Se shows fluorescence property. Nonlinear optical properties are investigated using the open aperture Z-scan, employing 100 fs laser pulses, at 800 nm. While cubic Se could not change the absorptive nonlinearity of silica, nonlinear transmission of amorphous Se doped silica is found to be considerably enhanced, which is likely to be dominated by the intensity-dependent three-photon absorption nonlinearity.

Chapter 4 describes the defects related emission and nonlinear optical properties of polyvinylpyrolidine capped CuS quantum dots and nanoparticles. Doped semiconductor nanostructures are important for NIR plasmonics with enhanced nonlinear optical properties in the NIR regime.

Structural characterizations show that CuS nanoparticles have a hexagonal crystal structure while CuS quantum dots exhibit both cubic and hexagonal phases. Microstructural studies from HRTEM reveal that quantum dots consist of dislocations, stacking faults and twins, which are direct consequences of coalescence and nanocrystal growth by the oriented attachment mechanism. Defects free CuS nanoparticles with smooth edges may nucleate through Ostwald ripening growth. The smaller crystallite size and cluster formation in CuS quantum dots are found to have considerable effects on high energy excitonic band and low energy plasmonic band with the existence of an emission band peaked at 339 nm wavelength. Further, the evolution of optical nonlinearities at near resonant excitonic band (532 nm, 5ns exciations) and plasmonic band (800 nm, 100 fs excitations) are discussed both in CuS nanoparticles and quantum dots. From fluence-dependent transmittance measurements, CuS quantum dots are found to have larger third order nonlinear optical coefficients with a relatively lower optical limiting threshold at both excitation regimes. In addition to microstructural studies, the optical and nonlinear optical characterizations provide further evidence for the presence of surface states and defects in CuS quantum dots.

Chapter 5 presents synthesis of silica hybridized CuS, Ag_2S, alloy and nanocomposites with tunable nonlinear optical properties. A simple, facile route developed for preparing silica hybridized CuS and Ag_2S quantum dots at room temperature is presented. Ag_2S can form Ag_2S-CuS (NCs) and its alloy with copper, which can be tailor-made through the concentration dependence of the growth kinetics. Their crystalline, structural and optical properties are discussed in detail and the optical limiting (OL) nature studied from fluence-dependent transmittance measurements employing short (5 ns) laser pulses at 532 nm is explained. The optical limiting efficiency can be tuned by changing the CuS concentration in Ag_2S/CuS nanoparticles, with pure Ag_2S nanoparticles exhibiting highest optical limiting efficiency. Their excellent optical

limiting properties indicate the possibilities of the design and fabrication of commercially viable optical limiters.

In **Chapter 6,** the ultrafast optical nonlinearity in semiconducting nanofillers doped polymer films having enhanced dielectric constant is explained. Polyvinyl acetate films doped with CuS, Ag_2S, Ag_2S-CuS nanocomposite and alloy nanoparticles are synthesized. Their structural, optical and dielectric properties are explored. Their dielectric constant and conductivity are found to be tuned by constituent nanocrystal stoichiometries of conducting fillers with PVA - Ag_2S films showing maximum enhancement. The ultrafast nonlinear optical properties investigated using the open aperture Z-scan, employing 100 fs laser pulses, at 800 nm, is discussed in detail. The optical limiting threshold can be tailored by changing the CuS concentration in the nanocomposites with maximum limiting efficiency for PVA-CuS films. These free standing PVA nanocomposite films show good optical limiting property and the nonlinear absorption is due to the combined effect of saturable and two-photon absorption.

Chapter 7 presents the general conclusions drawn from the work presented in the thesis, and some future perspectives.

The research work presented in the thesis has either been published in or communicated to reputed international journals and presented in various national/international seminars.

Research Papers Published /Communicated

1. K.A. Vishnumurthy, A. Vasudeva Adhikari, M.S. Sunitha, **K.A. Ann Mary**, Reji Philip, "Design and synthesis of a new thiophene based donor–acceptor type conjugated polymer with large third order nonlinear optical activity", Synth. Mater. 161 (2011) 1699.

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3. **K. A Ann Mary**, N. V Unnikrishnan, Reji Philip, "Ultrafast optical nonlinearity in nanostructured selenium allotropes", Chem. Phys. Lett. 588 (2013) 136.

4. Karthika S, **K. A Ann Mary**, Sunil Thomas, Cyriac Joseph, Unnikrishnan N V "Structural and spectroscopic studies of Sm^{3+}/CdS nanocrystallites in sol-gel TiO2 -ZrO2 matrix" J. Electron. Mater. 43 (2014) 447.

5. Arun Kumar K V, Sunil Thomas, **K. A Ann Mary**, Cyriac Joseph, Biju P R, Unnikrishnan N V "Dielectric and ac conductivity studies of ZnO/Eu^{3+}: titanosilicate matrix" AIP conf Proc. 1576 (2014) 209.

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7. K. A Ann Mary, E J Sonia Mary, Viji Vidyadharan, Reji Philip, N.V Unnikrishnan, "Thermo-optic nonlinearity of the laser dye LDS 867 under low power CW laser excitation" (accepted in IOP Conf Ser. Mater. Sci. Eng)

8. **K. A Ann Mary**, N. V Unnikrishnan, Reji Philip, "Facile One-Pot Synthesis of Silica-Hybridized Ag_2S-CuS Alloy/Nanocomposites with Tunable Nonlinear Optical Properties" (Submitted to Mater. Chem .Phys)

9. K. A Ann Mary, Sunil Thomas, Sajna M S, N. V Unnikrishnan, Reji Philip, "Enhanced dielectric constant of PVA films doped with semiconducting nanofillers" (Submitted to J. Phys. D: Appl. Phys.)

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11. Sajna M. S, Sunil Thomas, **Ann Mary K. A**, Cyriac Joseph, Biju P. R, N. V. Unnikrishnan, "Optical properties of Er^{3+} ions in multicomponent tellurite glasses" (Submitted to J. Lumin)

12. **K. A Ann Mary**, N. V Unnikrishnan, Reji Philip, "Ultrafast optical nonlinearity in CuS-Ag_2S PVA films" (under preparation).

13. **Ann Mary K.A**, Sonia Mary E.J, Reji Philip, "Modeling of thermal nonlinearity with Thermal Lens Model and Sheik Bahae formalism and occurrence of self phase modulation rings at low power laser beam" (under preparation).

14. **K. A Ann Mary**, N. V Unnikrishnan, Reji Philip, "Enhanced optical nonlinearity of Se doped silica in ultrafast (fs) and short-pulse (ns) excitations" (under preparation)

15. **K. A Ann Mary**, Sunil Thomas, Sajna M S, N. V Unnikrishnan, Reji Philip, "Fluorescence enhancement and quenching in Sm^{3+}/Se nanocrystallites doped silica matrix" (under preparation)

Research Papers Presented in National /International Seminars

1. **Ann Mary K.A**, Sonia Mary E.J, Reji Philip, "Thermo-optical nonlinearity in the laser dye Styryl 8 and $CuSO_4$ investigated by a low power laser beam", National Seminar at S.H College, 2011, Chalakudy.

2. **K A Ann Mary**, E J Sonia Mary, Viji Vidyadharan, Reji Philip, N.V Unnikrishnan, "Thermo-optic nonlinearity of the laser dye LDS 867 under low power CW laser excitation", ICMST 2012, Pala, Kottayam.

3. **K. A Ann Mary**, N. V Unnikrishnan, Reji Philip, "Synthesis and nonlinear optical properties of silica capped I-IV metal sulfides", Swadeshi Science Congress, 2013, Kottayam.

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5. Arun Kumar K V, **Ann Mary K A**, Biju P R and N V Unnikrishnan "Luminencemence enhancement in Ag nanoparticles/Eu^{3+} : SiO_2-TiO_2 matrices", National Laser Symposium (NLS-20), 2012, Anna University, Chennai.

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8. **K. A. Ann Mary**, Sajna M.S, Sunil Thomas, N. V. Unnikrishnan, Reji Philip, "Synthesis of silica capped CuS and Ag_2S nanoparticles and their nonlinear optical proeperties, Indo-German Conference, 2013 Trivandrum.

9. **K. A Ann Mary**, N. V Unnikrishnan, Reji Philip, "One pot synthesis of silica capped I-VI metal sulfides and their nonlinear optical properties, National Laser Symposium (NLS-22) 2014 Manipal.